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The University of Chicago.
Founded by JOHN D. ROCKEFELLER.

On Substituted Benzhydrol Derivatives and Bromcyanacetic Ether.

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE SCHOOLS OF ARTS, LITERATURE, AND SCIENCE, IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

DEPARTMENT OF CHEMISTRY.

By N. E. GOLDTHWAITE.

EASTON, PA.:
Press of the Chemical Publishing Co.
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PART I.

On Substituted Benzhydrol Derivatives.

Experiments on the isomeric dibromdiphenylmethanes, $(C_6H_4Br)_2{=}CH_2$, were undertaken with the object of determining, if possible, the position of the two bromine atoms in the benzene rings, and the relative amounts of the different isomers produced when diphenylmethane is brominated at a low temperature. The derivatives of the general formula, $(C_6H_4Br)_2{=}CHX$ (in which X = Br, OH, $OCOCH_3$, etc.), were studied with especial care as these compounds are of interest because of their low points of dissociation; they lose HX at temperatures varying from 165° to 300°, and are thus found to be perfectly analogous in their reactions to benzhydrol, benzhydrol ether, diphenylmethyl bromide, and benzylic acid, whose chemistry has been so carefully worked out by Nef.[2]

Paradibromdiphenylmethane, $(C_6H_4Br)_2{=}CH_2$.—The action of bromine on diphenylmethane has been studied only at high temperatures, when diphenylmethyl bromide[3] is formed. If, however, the action is carried out at low temperatures[4] and in the presence of iodine,[5] the bromine enters the benzene rings exclusively, and *p*-dibromdiphenylmethane (70 per cent) is produced together with small amounts of the corresponding *o*,*p*- and *o*-dibrom compounds. The exact method of work was as follows: A mixture of diphenylmethane[6] (100 grams) and iodine (10 grams—reaction goes as well with 5 grams)

[1] The work here described was performed during the years 1895–1897, under the direction of Dr. J. U. Nef, in the Kent Chemical Laboratory of the University of Chicago.

[2] Ann. Chem. (Liebig), **298**, 231–256.

[3] Friedel and Balsohn: Bull. soc. chim., **33**, 339, 589; Nef: Ann. Chem. (Liebig), **298**, 232.

[4] Jackson and Field: Am. Chem. J., **2**, 10.

[5] Beilstein: Ann. Chem. (Liebig), **143**, 370.

[6] Friedel and Crafts: Ann. chim. phys. [6], **1**, 478; Nef: Ann. Chem. (Liebig), **298**, 231; Radiewanski: Ber. d. chem. Ges., **27**, 3236.

was cooled to 0° in a large flask which was connected with a drop-funnel and with a reflux condenser, the latter being provided with a calcium chloride tube at its upper end. By means of the drop-funnel, 200 grams of bromine (2 mols.) were added drop by drop to the contents of the flask, the latter being shaken constantly. Hydrobromic acid gas was evolved rapidly. When all the bromine had been added, the flask with its contents, which had been kept cold with ice-water, was packed in ice for twelve hours. Subsequently, the very viscous reaction-product was poured into water and the resulting highly colored, heavy oil was extracted with ether. The ethereal solution was washed with sodium hydroxide and then treated with sulphurous acid to remove the iodine, and finally dried over calcium chloride. After distilling off the ether, the residual oil was distilled in a vacuum. It practically all boiled (93 to 96 per cent yield) with slight decomposition at 246°, 47 mm. pressure; at 224°, 22 mm. pressure, or 213°, 16 mm. pressure. The thick, nearly colorless, oily distillate readily solidified in part on cooling. The semi-solid was washed at the filter-pump with cold, low-boiling ligroin, when the oily isomers, consisting of the *o,p*- and probably the *o*-dibrom compounds, dissolved, together with a considerable portion of the crystalline *p*-dibrom compound, which was found to be the chief reaction-product. By distilling off the ligroin from the filtrate and treating the residual oil repeatedly in the manner above described, the latter compound was largely removed from the mixture and was obtained perfectly pure by subsequent recrystallizations from low-boiling ligroin. It was not found possible at this point to separate the *p*-dibrom compound completely from its oily isomers, nor to separate the *o,p*- and the *o*-dibromdiphenylmethanes from each other, yet by the oxidation, finally, of the oily mixture to the corresponding ketones, $(C_6H_4Br)_2{=}C{=}O$, and the subsequent separation of these by crystallization, the character of the isomeric products was established (see below).

Paradibromdiphenylmethane, whose constitution as a *p*-compound was proved by its conversion into *p*-dibrombenzophenone (see below), is a white, crystalline compound. It is

very soluble in ether, alcohol, benzene, glacial acetic acid, acetone, acetic ether, and carbon bisulphide. It is difficultly soluble in cold, low-boiling ligroin; hence this is the best solvent for its purification. After recrystallizing several times and subsequent drying in a vacuum over concentrated sulphuric acid, it melts sharply at 64°.

0.2025 gram substance gave 0.3568 gram CO_2 and 0.0635 gram H_2O.

0.2022 gram substance gave, by the Carius method, 0.2320 gram AgBr.

	Calculated for $(C_6H_4Br)_2=CH_2$.	Found.
C	47.85	48.04
H	3.06	3.48
Br	49.07	49.08

Paradibromdiphenylmethyl Bromide, $(C_6H_4Br)_2=CHBr$.—This compound was obtained by treating *p*-dibromdiphenylmethane with bromine at 150°.[1] The process was carried out with an apparatus similar to the one already described for the preparation of dibromdiphenylmethane. To *p*-dibromdiphenylmethane, heated to 150°, bromine (slightly more than 1 mol.) was added drop by drop, the containing flask being constantly shaken. Hydrobromic acid gas was evolved vigorously, and when all the bromine had been added the reaction was practically over. When cold, the light-brown, crystalline mass was broken up and water was added. The crystals were filtered off, thoroughly washed with water, dried, and then purified by recrystallizing from ether, or from ligroin, or from a mixture of the two.

It should be noted here that the mother-liquors left from the purification of *p*-dibromdiphenylmethyl bromide invariably gave off hydrobromic acid gas, no matter how carefully the ether or ligroin solution had been freed previously from this acid. The mother-liquors also always deposited crystals of *p*-dibrombenzophenone, $(C_6H_4Br)_2=C=O$ (m. p. 172° to 173°). These crystals, which are long, flat, and thin (sometimes in plates), with obliquely cut ends, possess a pearly lus-

[1] Friedel and Balsohn: Bull. soc. chim., **33**, 339.

ter, and can thus readily be detected among the fine, needle-like crystals of *p*-dibromdiphenylmethyl bromide. They can also be distinguished from the bromide crystals by the fact that they give no reaction with concentrated sulphuric acid, while the latter give a deep-red color with this reagent.

Paradibromdiphenylmethyl bromide is a white, crystalline compound, very soluble in alcohol (by which it is slowly decomposed), benzene, and chloroform; less soluble in ether and ligroin. Hence, the two latter solvents are best used for its purification. It melts at 106° to 107°.

0.2275 gram substance gave 0.3250 gram CO_2 and 0.0538 gram H_2O.

0.1940 gram substance gave, by the Carius method, 0.2680 gram AgBr.

	Calculated for $(C_6H_4Br)_2=CHBr$.	Found.
C	38.52	38.96
H	2.22	2.62
Br	59.25	59.09

Paradibromdiphenylmethyl bromide, as well as the corresponding benzhydrol derivatives, gives a deep-red color with concentrated sulphuric acid.[1] It cannot be distilled even under diminished pressure because of its very low point of dissociation. On heating the compound to 165° in absence of air, hydrobromic acid escapes and *p*-tetrabromtetraphenylethylene, $(C_6H_4Br)_2=C=C=(C_6H_4Br)_2$, is formed. When heated above its melting-point in a stream of dry air, it is largely oxidized to *p*-dibrombenzophenone, $(C_6H_4Br)_2=C=O$. If treated with water under proper conditions, *p*-dibrombenzhydrol ether, $(C_6H_4Br)_2=CH-O-CH=(C_6H_4Br)_2$, is produced. Treatment with sodium acetate leads to the formation of *p*-dibrombenzhydrol acetate,

$$(C_6H_4Br)_2=CH-O-CO-CH_3,$$

while with sodium ethylate or with ethyl alcohol, *p*-dibrombenzhydrol ethyl ether,

$$(C_6H_4Br)_2=CH-O-C_2H_5,$$

[1] Nef: Ann. Chem. (Liebig), 298, 241.

results. All these reactions are self-evident from the standpoint of a methylene dissociation.[1]

Two attempts to isolate *p*-dibromdiphenylmethylene bromide, $(C_6H_4Br)_2{=}CBr_2$, through treating *p*-dibromdiphenylmethyl bromide with bromine (1 mol.) at 150°, were unsuccessful. On treating the reaction-product with water, *p*-dibrombenzophenone (m. p. 172° to 173°) was obtained quantitatively. Friedel and Balsohn[2] report that they were unable to purify the corresponding diphenylmethane dibromide, $(C_6H_5)_2{=}CBr_2$, and state that it gave benzophenone when heated to 150° with water. Apparently, *p*-dibromdiphenylmethylene bromide is so unstable that when it is merely brought into contact with water it is decomposed in an analogous manner.

Paradibrombenzophenone, $(C_6H_4Br)_2{=}CO$.—This compound was repeatedly produced in small quantities as a side-product in the experiments on *p*-dibromdiphenylmethane and its derivatives. A carbon and hydrogen analysis of this ketone was carried out when it was obtained as a decomposition-product through heating *p*-dibrombenzhydrol (see below), and it was analyzed for bromine when it was formed as a decomposition-product through heating *p*-dibrombenzhydrol ethyl ether (see below). The results of these analyses are here given :

0.2047 gram substance gave 0.3441 gram CO_2 and 0.0450 gram H_2O.

0.2690 gram substance gave, by the Carius method, 0.2967 gram AgBr.

	Calculated for $(C_6H_4Br)_2{=}CO$.	Found.
C	45.88	45.84
H	2.33	2.44
Br	47.05	47.18

This ketone was obtained quantitatively by oxidation of *p*-dibrombenzhydrol, $(C_6H_4Br)_2{=}CHOH$, by means of chromic acid. To a weighed quantity of this alcohol (see below)

[1] Nef : Am. Chem. (Liebig), **298**, 231–241.

[2] Bull. soc. chim., **33**, 337–339.

dissolved in glacial acetic acid, the calculated quantity of finely powdered potassium bichromate was added gradually, and the mixture heated for some time. The oxidation was known to be complete when a drop of the solution no longer gave a red color with concentrated sulphuric acid. On addition of water, a crystalline compound was precipitated, which, when filtered, washed, dried, and recrystallized from ligroin, showed the characteristic, slender, flat crystals which have been described above. It melted at 172° to 173°, and it gave no red color with concentrated sulphuric acid. This ketone was likewise quantitatively produced by oxidizing *p*-dibromdiphenylmethane in glacial acetic acid solution with chromic acid.

That the compound produced in all these reactions is *p*-dibrombenzophenone, is proved by its identity with *p*-dibrombenzophenone which has been prepared in other ways by E. Hofmann,[1] by Schöpf,[2] and by Cathcart.[3] The compound obtained in the present case was, furthermore, converted into the oxime (following Schäfer's[4] method for the preparation of *p*-monobrombenzophenone oxime), and a compound melting at 150° to 152° was obtained.[5] This oxime, when crystallized from ligroin, appeared in two distinct forms, each melting sharply at 150° to 152°. One modification consisted of long, slender, needle-like crystals[6] and the other of flat, rhombic ones. When the latter were redissolved in ligroin and the solution "seeded" with the needle-like crystals, all of the compound was obtained in the form of needles, with the melting-point 150° to 152°. These two crystalline forms of this oxime have not been previously mentioned.

When *p*-dibrombenzophenone was reduced in acid solution, some *p*-dibrombenzhydrol (m. p. 115° to 116°) was obtained, and also a crystalline compound (m. p. 158° to 161°), which may have been the corresponding pinacone,[7] was isolated, but this was not further investigated.

[1] Ann. Chem. (Liebig), **264**, 162.
[2] Ber. d. chem. Ges., **24**, 3767.
[3] *Ibid.*, **25**, 3302.
[4] Ann. Chem. (Liebig), **264**, 154.
[5] Cathcart: Ber. d. chem. Ges., **25**, 3202.
[6] Hofmann: Ann. Chem. (Liebig), **264**, 164.
[7] Linnemann: *Ibid.*, **133**, 27.

Orthoparadibrombenzophenone, $(C_6H_4Br)_2{=}CO$.—The isomeric dibromdiphenylmethanes obtained by brominating diphenylmethane at a low temperature, consist, as stated above, of about 70 per cent of the crystalline *p*-dibrom compound; about 27 per cent is the *o*,*p*-compound, while the remainder is probably the *o*-dibrom derivative. This was proved as follows: A mixture of 150 grams of the oily dibromdiphenylmethanes, from which the *p*-compound had been removed as completely as possible in the manner already described, was transformed successively in a manner analogous to that described for the conversion of *p*-dibromdiphenylmethane into the corresponding bromides, $(C_6H_4Br)_2{=}CHBr$, then into the acetates, $(C_6H_4Br)_2{=}CH{-}O{-}CO{-}CH_3$, and into the alcohols, $(C_6H_4Br)_2{=}CH{-}OH$. As none of these compounds could be obtained in a crystalline condition, the alcohols were finally oxidized to the corresponding ketones by means of chromic acid in glacial acetic acid solution. Thus, a mixture of 90 grams of oily ketones was obtained from which 7 grams of *p*-dibrombenzophenone (m. p. 170° to 172°) separated out on cooling. These oily ketones boiled smoothly at 226° and 14 mm. pressure; under considerable decomposition at 323°, ordinary pressure. After some weeks' standing in a cool place, a crystalline compound (60 grams) was deposited slowly and was separated by filtration. This compound, when recrystallized from low-boiling ligroin, appeared in groups of large, flat crystals having squarely cut ends, and melted at 50° to 52°. That this body is identical with *o*,*p*-dibrombenzophenone obtained by Heidenreich[1] from *o*-brombenzoyl chloride and brombenzene in presence of aluminium chloride, was proved by converting a portion of it into its oxime (m. p. 140° to 142°); this oxime was thereupon converted into the corresponding indoxazene compound, which crystallizes in white needles (m. p. 132° to 133°). These transformations were carried out according to Heidenreich's method. The melting-points and other properties of the compounds produced correspond to those given by this investigator.

[1] Ber. d. chem. Ges., **27**, 1453.

A bromine determination of the *p*-bromphenyl indoxazene obtained gave the following figures:

0.1538 gram substance gave, by the Carius method, 0.1053 gram AgBr.

	Calculated for $C_{13}H_8BrNO$.	Found.
Br	29.19	29.25

An attempt was made to obtain *o,p*-dibrombenzhydrol by reducing *o,p*-dibrombenzophenone with sodium amalgam. The experiment was carried out as in the reduction of the *p*-dibrom ketone, but instead of obtaining the *o,p*-dibrombenzhydrol sought, a partial elimination of the bromine was effected. Through a quantitative examination of the solution in which the reduction had been carried out, it was proved that 11 per cent of the bromine had been removed from the weight of *o,p*-dibrombenzophenone used.

It seemed probable that the oil from which the *o,p*-dibrombenzophenone crystals had been separated must be the corresponding *o*-dibrom ketone. But when an attempt was made to form its oxime, a crystalline compound (2.7 grams out of a possible 5.3 grams) which melted at 140° to 141° was obtained. This body, when heated with sodium ethylate in a sealed tube, gave an indoxazene which melted at 128° to 129°. As these melting-points correspond so closely with those of *o,p*-dibrombenzophenone oxime and of *p*-bromphenyl indoxazene, respectively, it must be inferred that at least 50 per cent of the oil consisted of *o,p*-dibrombenzophenone.

Paratetrabromtetraphenylethylene, $(C_6H_4Br)_2{=}C{=}C{=}(C_6H_4Br)_2$.—It has been stated already that when *p*-dibromdiphenylmethyl bromide is heated hydrobromic acid escapes, and if no air is present *p*-tetrabromtetraphenylethylene is formed quantitatively, as follows:

$$2(C_6H_4Br)_2 : CHBr \rightarrow 2(C_6H_4Br)_2 : C \rightleftarrows$$
$$+ 2HBr \rightarrow (C_6H_4Br)_2 : C : C : (C_6H_4Br)_2 + 2HBr.$$

If, however, air is present, the methylene derivative may be partially or entirely oxidized to the ketone:

$$(C_6H_4Br)_2 : CHBr + O \rightarrow (C_6H_4Br)_2 : C \rightleftarrows$$
$$+ O + HBr \rightarrow (C_6H_4Br)_2 : C : O + HBr.$$

Thus, when a stream of dry air was drawn through molten *p* dibromdiphenylmethyl bromide, not more than half the resulting product consisted of the polymerized ethylene derivative, while the remainder was *p*-dibrombenzophenone (m. p. 172° to 173°). This explains why solutions containing *p*-dibromdiphenylmethyl bromide oxidize spontaneously on standing at the ordinary temperature, with loss of hydrobromic acid, to the corresponding *p*-dibrombenzophenone.

It was found that *p*-tetrabromtetraphenylethylene was formed most smoothly when *p*-dibromdiphenylmethyl bromide was heated in a distilling-bulb so arranged that a stream of dry air was drawn through the neck and arm of the bulb, but not through the molten bromide. Under these conditions, the bromide begins to lose hydrobromic acid gas as soon as the temperature of the bath reaches 165°. The temperature was finally raised to 230°–240° and kept there for some hours. The resulting deeply colored residue was dissolved in benzene and thoroughly digested with animal charcoal. Finally the benzene was distilled off and the residue dissolved in hot alcohol; on cooling, tiny, white, needle-like crystals separated out. The presence of any *p*-dibrombenzophenone was readily detected by examination of the first crystals which appeared, and this body was removed mechanically if found. The ethylene derivative, after several recrystallizations from glacial acetic acid, and careful drying for some days in a vacuum over fused caustic potash, melted sharply at 248°.

0.2378 gram substance gave 0.4174 gram CO_2 and 0.0559 gram H_2O.

	Calculated for $(C_6H_4Br)_2=C=C=(C_6H_4Br)_2$.	Found.
C	48.14	47.87
H	2.47	2.61

A molecular weight determination by the freezing-point method, using benzene as a solvent, gave the following results:

	I.	II.
Weight of benzene	30 grams	30 grams
" " compound	0.2110 grams	0.3810 grams
Depression of freezing-point	0°.055	0°.110
Molecular weight found	638.1	577.3
" " calculated for $(C_6H_4Br)_2 : C : C : (C_6H_4Br)_2$		648

An attempt to form the corresponding ethane derivative through reduction of this ethylene compound by means of zinc and acetic acid was unsuccessful. The original ethylene compound (m. p. 248°) was entirely recovered. This compound also refuses to take up bromine.

Paratetrabromtetraphenylethylene is possibly also one of the decomposition-products of *p*-dibrombenzhydrol through heat (see below).

Paradibrombenzhydrol Acetate, $(C_6H_4Br)_2{=}CH{-}O{-}CO{-}CH_3$. — When *p*-dibromdiphenylmethyl bromide is treated with sodium acetate (1.5 mols.) in glacial acetic acid solution, the corresponding *p*-dibrombenzhydrol acetate is formed.[1] Five such experiments with quantities of the bromide varying from 5 grams to 23 grams were carried out, and in each case nearly quantitative yields were obtained by heating only a few minutes on an asbestos plate under a reflux condenser in order to complete the reaction. On addition of water, an oil separated out, which was extracted with ether, washed with an alkali, and dried over calcium chloride. The ether was distilled off and the oily residue was dissolved in hot ligroin ; on cooling, very short, fine, needle-like crystals, which melted at 70° to 72°, were obtained. The compound burned with some difficulty but a carbon and hydrogen analysis gave the following results :

0.2077 gram substance gave 0.3532 gram CO_2 and 0.0645 gram H_2O.

	Calculated for $(C_6H_4Br)_2{=}CH{-}O{-}CO{-}CH_3$.	Found.
C	46.87	46.38
H	3.12	3.44

Paradibrombenzhydrol acetate is very soluble in most or-

[1] Friedel and Balsohn : Bull. soc. chim., **33**, 338 ; Vincent : *Ibid.*, **35**, 304.

ganic solvents, but less so in low-boiling ligroin. With concentrated sulphuric acid, it gives the characteristic deep-red color given by the bromide under similar conditions. When heated with water or with alcoholic potash it gives *p*-dibrombenzhydrol.

Paradibrombenzhydrol, $(C_6H_4Br)=CHOH$.—This compound was best prepared by the action of alcoholic potash (1.5 mols.) upon *p*-dibrombenzhydrol acetate. The reaction was completed in the cold after standing a few hours, or on heating, in a few minutes. A small amount of *p*-dibrombenzophenone usually crystallized out from this alcoholic solution and was separated by filtration. The alcoholic filtrate, when poured into water, gave a fine, white, crystalline precipitate of *p*-dibrombenzhydrol, which was purified by recrystallizing from a mixture of ether and ligroin. Very long, fine, white needles, melting at 115° to 116°, were obtained.

0.2007 gram substance gave 0.3335 gram CO_2 and 0.0574 gram H_2O.

	Calculated for $(C_6H_4Br)_2=CHOH$.	Found.
C	45.61	45.32
H	2.92	3.17

Paradibrombenzhydrol was also obtained by the action of water in slightly diluted acetic acid solution upon *p*-dibrombenzhydrol acetate.

Paradibrombenzhydrol is very soluble in ether, alcohol, and acetic acid, but very little soluble in ligroin. When ground in an agate mortar, it shows remarkable electric properties. With concentrated sulphuric acid it gives the characteristic deep-red color already mentioned. When treated with ethyl alcohol in presence of concentrated sulphuric acid, *p*-dibrombenzhydrol ethyl ether is formed, while with benzene in presence of the same acid, *p*-dibromtriphenylmethane results. Both of these compounds will be described below. With oxidizing agents, *p*-dibrombenzophenone is produced.

Paratetrabromtetraphenylethane,
$(C_6H_4Br)_2=CH—CH=(C_6H_4Br)_2$.—The behavior of benzhydrol at its dissociation-point (300°) has been thoroughly in-

vestigated by Nef.[1] The following experiments show that when *p*-dibrombenzhydrol is heated to its dissociation-point (162°), analogous reactions take place, except that in one case a fair amount of *p*-tetrabromtetraphenylethylene was also obtained.

a. Paradibrombenzhydrol (4 grams), when heated in a distilling-bulb in a metal-bath, began to give off water at 162°. The temperature of the bath was gradually raised to 250°, when the reaction was complete. The fused mass, on heating to 300° for five minutes longer, grew dark in color, therefore the operation was discontinued. The mass was digested with hot benzene, which left a portion insoluble in ether, alcohol, glacial acetic acid, carbon bisulphide, acetic ether, acetone, chloroform, carbon tetrachloride, but soluble in hot nitrobenzene. On recrystallizing from this solvent, a compound (1.5 grams), which melted above 300° and which gave no color-reaction with concentrated sulphuric acid, was obtained. An analysis proved this body to be *p*-tetrabromtetraphenylethane.

0.1961 gram substance gave 0.3442 gram CO_2 and 0.0531 gram H_2O.

0.1938 gram substance gave, by the Carius method, 0.2224 gram AgBr.

	Calculated for $(C_6H_4Br)_2=CH-CH=(C_6H_4Br)_2$.	Found.
C	48.00	47.87
H	2.77	3.00
Br	49.23	49.09

On examination, the benzene solution, decolorized by digesting with animal charcoal, was found to contain a crystalline compound little soluble in alcohol, from which it was recrystallized till pure. Glistening, flat, slender crystals (0.9 gram), which melted at 172° to 173°, were obtained. This compound, through its properties and analysis (see above), was proved to be *p*-dibrombenzophenone.

The mother-liquors left from recrystallizing *p*-dibrombenzophenone were found to contain a small amount of a crystal-

[1] Ann. Chem. (Liebig), **298**, 241.

line compound melting at 85°—probably a mixture of *p*-dibromdiphenylmethane and *p*-dibrombenzophenone.

b. Paradibrombenzhydrol (2 grams) was placed in a distilling-bulb connected with a U-tube, and a stream of dry air was drawn through the apparatus, while the metal-bath was heated quickly to 250° and kept there for five minutes. Water condensed in the delivery-tube and in the U-tube. The white, crystalline residue was extracted with ether. After adding ligroin and distilling off the ether, hexagonal, transparent crystals of *p*-dibrombenzhydrol ether (see below), melting at 150° to 152°, were deposited.

c. Paradibrombenzhydrol (5 grams) was heated for forty minutes (bath at 300°) in a distilling-bulb provided with a thermometer, and so arranged that a distillate and any evolved gas could be collected. Water distilled off, but no gas was obtained. The crystalline residue was completely dissolved in hot benzene. On distilling off this benzene and redissolving in alcohol, the following compounds were separated by fractional crystallization: *p*-Dibrombenzophenone (1.5 grams) melting at 172° to 173°, *p*-dibromdiphenylmethane (0.4 gram) melting at 63° to 64°, and a compound (0.4 gram) melting at 252° to 254°, which, from its small, needle-like crystals, its solubilities and its melting-point (though this was slightly higher than that given above for the pure substance), was thought to be *p*-tetrabromtetraphenylethylene.

d. In a small flask through which a stream of dry carbon dioxide was constantly drawn and which was arranged under a reflux condenser, *p*-dibrombenzhydrol (5 grams) was heated to 300° for eight hours. The resulting crystalline residue was nearly all dissolved in hot alcohol, and from this solution the following compounds were separated by fractional crystallization: *p*-Dibrombenzophenone (0.6 gram) melting at 172° to 173°, a trace of the body described under *c*, melting at 250° to 254°, also mixtures melting from 120° to 170°, from 170° to 230°, from 160° to 164°. The small residue insoluble in alcohol, left in the bulb, melted at 275°, but there was not a sufficient amount for further purification. It is probable that *p*-dibrombenzophenone, *p*-dibrombenzhydrol ether, possi-

bly *p*-tetrabromtetraphenylethylene, and the corresponding ethane derivative were present in these mixtures, but this was not proved.

Paradibrombenzhydrol Ether, $(C_6H_4Br)_2{=}CH{-}O{-}CH{=}(C_6H_4Br)_2$.—The experiments just described prove that when *p*-dibrombenzhydrol is heated, *p*-dibrombenzhydrol ether is first formed, but since this ether has a dissociation-point only very slightly higher than its alcohol, it cannot, therefore, be isolated in quantity by this process. The best method for the preparation of this compound is to heat *p*-dibromdiphenylmethyl bromide with water.[1] Five grams of the bromide with 20 cc. of water and the amount of calcium carbonate necessary to destroy the hydrobromic acid formed, were heated in a sealed tube at 120° for twenty hours. The residue, which was insoluble in water, was recrystallized from low-boiling ligroin. Two compounds crystallized out, and these were separated mechanically. One (3.35 grams) consisted of masses of short crystals radiating from a center and melting at 148° to 150°; the other (0.2 gram consisted of the long, slender, flat crystals of *p*-dibrombenzophenone, melting at 172 to 173°. On recrystallizing the main reaction-product from ligroin, and finally from alcohol, it melted at 155° to 156°.

0.2248 gram substance gave 0.3834 gram CO_2 and 0.0577 gram H_2O.

0.2152 gram substance gave, by the Carius method, 0.2426 gram AgBr.

	Calculated for $(C_6H_4Br)_2{=}CH{-}O{-}CH{=}(C_6H_4Br)_2$.	Found.
C	46.84	46.51
H	2.70	2.85
Br	48.04	48.18

Paradibrombenzhydrol ether is extremely soluble in benzene and in chloroform; less so in alcohol, ether, and ligroin. It gives a deep-red color with concentrated sulphuric acid. That it is not acted upon by boiling with alcohol was proved by heating it (1 gram) with alcohol (15 cc.) in a sealed tube

[1] Nef: Ann. Chem. (Liebig), **298**, 232.

at 100° for thirty hours. The compound was entirely recovered unchanged. On the other hand, heating with acetic acid, very readily converts it, as well as the corresponding *p*-dibrombenzhydrol, into *p*-dibrombenzhydrol acetate—a fact which, in view of the low point of dissociation of both this ether and its alcohol, is easily understood.

Paradibrombenzhydrol Ethyl Ether, $(C_6H_4Br)_2=CH—O—C_2H_5$.—This compound was formed by allowing an alcoholic solution of *p*-dibromdiphenylmethyl bromide to stand in the cold; but the bromide, in the presence of a molecular quantity of cold alcoholic sodium ethylate reacted almost instantly. To insure complete reaction, the mixture was heated a short time; on pouring it into water, an oil separated out which was extracted with ether. This was well washed and then dried over calcium chloride. After distilling off the ether, the residual oil, when distilled in a stream of carbon dioxide, boiled at 228° at 16 mm. pressure. All attempts to distil this oil in presence of air, even under diminished pressure, resulted in the formation of some *p*-dibrombenzophenone.

0.2642 gram substance gave 0.4685 gram CO_2 and 0.0967 gram H_2O.

0.3650 gram substance gave, by the Carius method, 0.3692 gram AgBr.

	Calculated for $(C_6H_4Br)_2=CH—O—C_2H_5$.	Found.
C	48.64	48.36
H	3.78	4.06
Br	43.24	43.25

Paradibrombenzhydrol ethyl ether is a thick, colorless oil with a characteristic, not unpleasant, odor. With concentrated sulphuric acid it gives a deep-red color.

That *p*-dibrombenzhydrol ethyl ether can also be obtained from *p*-dibrombenzhydrol or its corresponding ether, by means of ethyl alcohol and concentrated sulphuric acid, was proved by experiment. This reaction is self-evident, in view of the experiments of Linnemann[1] and Nef,[2] and in view of the low dissociation-point of these substances.

[1] Ann. Chem. (Liebig), **133**, 17.

[2] *Ibid.*, **298**, 255.

Behavior of p-Dibrombenzhydrol Ethyl Ether on Heating.— Paradibrombenzhydrol ethyl ether has a low dissociation-point. It breaks down at 300° into ethyl alcohol, ethylene (?), *p*-dibrombenzophenone, and *p*-dibromdiphenylmethane. The ether (6.5 grams), placed in a small distilling-bulb which was connected with a second distilling-bulb (receiver) and an azotometer, was heated in a metal-bath to 300° for three hours, when the reaction was complete. A small amount of liquid (b. p. 110°) distilled into the receiver, and at the same time 120 cc. of gas were collected in the azotometer. This gas, which burned with a smoky flame, was probably ethylene. The distillate separated into two layers, one, a a thin liquid, which, when redistilled, came over between 65° to 78° and gave the iodoform test, and was, therefore, probably ethyl alcohol; the other, an oil which had a wintergreen odor and which completely decomposed when an attempt was made to redistil it. The highly-colored crystalline residue left in the distilling-bulb was dissolved entirely in benzene and the solution was decolorized by digesting with animal charcoal. After distilling off the benzene, the residue was dissolved in alcohol. From this solution *p*-dibrombenzophenone (2 grams), melting at 172° to 173°, and *p*-dibromdiphenylmethane (0.6 gram), melting at 62° to 64°, were separated by fractional distillation; the melting-points are those obtained after recrystallizing from low-boiling ligroin.

The result of a bromine determination of the *p*-dibrombenzophenone here obtained has been given above.

Paradibromtriphenylmethane, $(C_6H_4Br)_2{=}CH{-}C_6H_5$.— Paradibrombenzhydrol, treated with benzene and concentrated sulphuric acid, gives *p*-dibromtriphenylmethane.[1] A solution of *p*-dibrombenzhydrol (3 grams) in benzene (50 cc.) was treated with concentrated sulphuric acid (15 cc.). After standing twelve hours in the cold, the highly-colored benzene solution was decanted from the acid, well washed, and then dried over calcium chloride. On distilling off the benzene, a thick oil with a yellowish-green fluorescence was left. It solidified at the end of ten days. The compound distilled

[1] Nef: Ann. Chem. (Liebig), 298, 254.

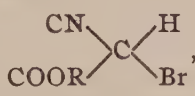
without decomposition at 260°, 15 mm. pressure., but still showed a yellowish-green fluorescence. It was found to be remarkably soluble in all organic solvents, but was finally purified by dissolving in alcohol and digesting repeatedly with animal charcoal. The alcoholic solution gave, on adding water, nearly a gram of a compound crystallizing in very fine, almost white, needles, and melting sharply at 100°.

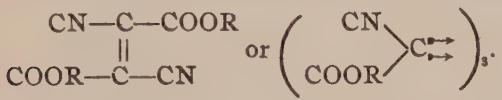
0.2141 gram substance gave 0.4426 gram CO_2 and 0.0687 gram H_2O.

0.1980 gram substance gave, by the Carius method, 0.1850 gram AgBr.

	Calculated for $(C_6H_4Br)_2=CH-C_6H_5$.	Found.
C	56.71	56.38
H	3.48	3.56
Br	39.80	39.94

PART II.

On Bromcyanacetic Ether,  , *and Its Conversion by Loss of Hydrobromic Acid into Dimolecular or Trimolecular Cyanmethylenecarboxylic Ether*,



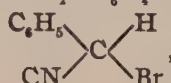
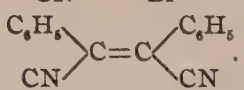
The main results of this work on bromcyanacetic ether have already been tabulated briefly by Nef.[1] It has since been sharply proved by him[2] that all primary and secondary alkyl haloids react with various reagents because they are partially dissociated, *i. e.*, alkylidene and HX particles are present, and the speed of the reaction[3] of alkyl haloids depends solely upon the number of such dissociated particles present at a given temperature. Thus, *p*-dibromdiphenylmethyl bromide, whose dissociation-point lies at about 165°, reacts instantly with alcoholic sodium ethylate, or slowly with alcohol, in the

[1] Ann. Chem. (Liebig), **298**, 258.

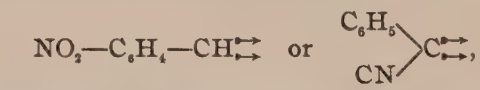
[2] *Ibid.*, **309**, 126; **318**, 316.

[3] In this way I believe the percentage of dissociation at various temperatures may be determined as accurately as the percentage of ionization of electrolytes by the conductivity method. J. U. Nef.

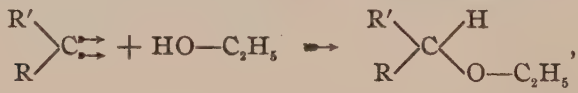
cold, whereas ethyl iodide, dissociation-point about 450°, reacts very slowly with alcoholic sodium ethylate in the cold and not at all with alcohol alone at 100°. At 150°, however, ethyl ether is formed.

There are some substituted alkyl haloids, however, as pointed out by Nef,[1] which show a very peculiar behavior when treated with alcoholic sodium ethylate or other so-called double decomposition reagents. Thus, *o*- and *p*-nitrobenzyl chloride give, in marked contrast to benzyl chloride, by treatment with alcoholic potash (or sodium ethylate) no trace of an ether, $NO_2—C_6H_4—CH_2—O—C_2H_5$ (or only small amounts),[2] but quantitative or relatively large amounts of the stilbene derivatives, *o*- and *p*-$NO_2—C_6H_4—CH=CH—C_6H_4—NO_2$. Brombenzyl cyanide,  , gives, on similar treatment, dicyanstilbene,  .

These results can only be understood, as pointed out by Nef, on the basis that the methylene residues, which become free when HX is removed by the alkali,



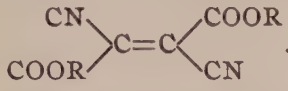
in these cases unite, in part or entirely, with each other to give the olefine derivatives mentioned above; whereas, ordinarily, the alkylidene residues absorb the reagent (alcohol, etc.) set free, or present as such, to give an addition-product,

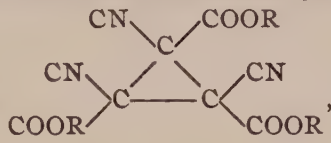
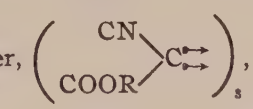


Bromcyanacetic ether is another such compound. It gives, as will be seen from what follows, on treatment with sodium, aniline, the sodium salts of malonic ether, and of cyan- and acetoacetic ether, a large amount (up to 67 per cent) of a crystalline compound (m. p. 120° to 122°), which, in view of

[1] Ann. Chem. (Liebig), **298**, 229, 257–260.

[2] Thiele: *Ibid.*, **305**, 103.

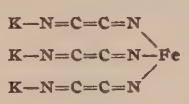
the facts tabulated above, would naturally be regarded as dicyanfumaric ether, *i. e.*, dimolecular cyanmethylenecarboxylic ether,  .

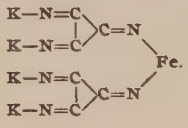
In 1900, Errara and Perciabosco[1] published a paper on the action of halogens on sodium cyanacetic ether. They found that this ether is converted by iodine, or bromine, into a crystalline compound melting at 119°, and they also obtained the same compound through the action of sodium cyanacetic ether upon bromcyanacetic ether. The compound is obviously identical with that mentioned above and obtained in various ways, as indicated, from bromcyanacetic ether. These observers consider that the compound under discussion is tricyantrimethylenetricarboxylic ether,  , *i. e.*, trimolecular cyanmethylenecarboxylic ester,  , and this is very probable because of its conversion by saponification and subsequent loss of carbon dioxide[2] into known trimethylene tri- and tetracarboxylic acids. They also give molecular weight determinations confirming this conclusion—which, however, are to be regarded as uncertain[3] (see below).

[1] Ber. d. chem. Ges., **33**, 2978.

[2] Scacherl: Ann. Chem. (Liebig), **229**, 89; Büchner: *Ibid.*, **284**, 197.

[3] Should further investigations, which I intend to make in the near future, confirm the formula of Errara and Perciabosco, it should be emphasized that this is one of the few instances yet known in which a methylene derivative polymerizes to a trimolecular modification (cf. polymeric fulminic acid, Ann. Chem. (Liebig), **280** 316). Azulmic acid, $(CNH)_x$, the polymerized isocyanides, $(RNC)_x$, the polymeric phenyl- and diphenylmethylenes, $(C_6H_5CH)_x$, $[(C_6H_5)_2C]_x$, are unquestionably all very complex polymers. Finally, I have on the basis of my bivalent carbon work for the past eight years, given in my lectures (cf. also Ann. Chem. (Liebig), **298**, 215, 313) the following very probable formulas to potassium ferri- and ferrocyanide, respectively:





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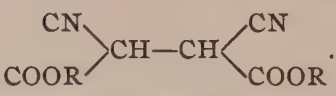
Finally, it should be mentioned that Thorpe and Young[1] have recently obtained a crystalline substance, melting at 120°, from sodium cyanacetic ether and iodine, to which they give the formula  . This is obviously identical with the dimolecular or trimolecular cyanmethylenecarboxylic ester under discussion. The analytical data given by Thorpe and Young must therefore be erroneous.

Preparation of Bromcyanacetic Ether.—This compound was prepared by adding bromine (1 mol.) slowly to cyanacetic ether which was heated in a bath at 150°, care being taken to avoid access of moisture. The crude reaction-product was distilled directly under reduced pressure. A 60 to 75 per cent yield was obtained.

Bromcyanacetic ether is a colorless oil with a somewhat piercing odor, boiling at 110° to 112°, at 18 mm. pressure, and between 195° to 200° at ordinary pressure, but with considerable decomposition. Treated with aqueous iodide of potassium, iodine is at once set free in the cold—a reaction frequently used as a test for this compound.

0.3348 gram substance gave 0.3839 gram CO_2 and 0.0940 gram H_2O.

0.3228 gram substance gave 21 cc. N at 18° and 743.7 mm. pressure.

0.1976 gram substance gave, by the Carius method, 0.1923 gram AgBr.

	Calculated for $C_5H_6NO_2Br$.	Found.
C	31.25	31.26
H	3.12	3.11
N	7.29	7.39
Br	41.66	41.41

Conversion of Bromcyanacetic Ether into Di- or Tri-molecular Cyanmethylenecarboxylic Ester.

a. By Means of Sodium.—Bromcyanacetic ether in benzene (or ethereal) solution reacted at once in the cold when treated

[2] J. Chem. Soc. (London), 77, 937.

with sodium (1 or 2 mols.) in the form of fine wire. On digesting the salt residue with hot benzene the benzene filtrates gave, on concentration and cooling, a 60 per cent yield of polymeric cyanmethylenecarboxylic ether, melting at 120° to 124°.

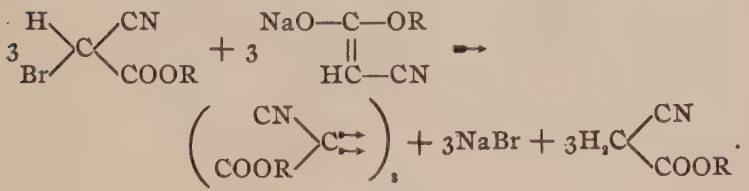
0.2193 gram substance gave 0.4325 gram CO_2 and 0.0905 gram H_2O.

0.2058 gram substance gave 0.4024 gram CO_2 and 0.0871 gram H_2O.

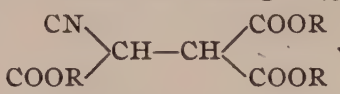
0.2008 gram substance gave 22.5 cc. N at 17° and 747.5 mm. pressure.

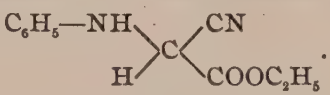
	Calculated for $\left(\begin{smallmatrix} CN \\ COOR \end{smallmatrix}\!\!>\!C\!\rightleftarrows\right)_x$.	Found. I.	Found. II.
C	54.05	53.78	53.32
H	4.50	4.58	4.70
N	12.61	12.82	....

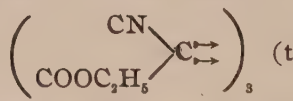
b. By Means of Sodium Cyanacetic Ether.—Five grams of sodium cyanacetic ether, suspended in absolute ether, were slowly treated in the cold with an ethereal solution of 7.1 grams (1 mol.) of bromcyanacetic ether and the mixture finally heated for four hours under a reflux condenser. Three and two-tenths grams of cyanacetic ether (80 per cent of the theory) boiling at 204°, and 2.7 grams of cyanmethylenecarboxylic ether (67 per cent yield), melting at 120° to 122°, were obtained as reaction-products:



c. By Means of Sodium Acetoacetic Ether and of Sodium Malonic Ether.—These reactions were not carried out quantitatively and therefore need repetition. The operations took place in absolute ethereal solutions and were accomplished, especially in the latter case, with considerable evolution of

heat. In the first case the formation of much free acetoacetic ether, as well as of polymeric cyanmethylenecarboxylic ester (40 per cent yield), melting at 120° to 122°, was unquestionably established. In the latter case, some of the polymeric methylene derivative (7 per cent) melting at 120° was isolated. Besides this a small amount of a crystalline compound, volatile with steam and melting at 45° to 47°, which may possibly be  was obtained.

d. By Means of Aniline.—Bromcyanacetic ether and aniline (1.5 mols.), in ethereal solution, reacted on each other in the cold. After standing forty-eight hours, a yield of 25 per cent of the theoretical amount of polymerized cyanmethylenecarboxylic ester (119° to 120°) was obtained. The other products formed, besides phenylammonium bromide, were a substance with odor of bromcyanogen, and a crystalline compound melting at 57°. The latter may possibly be the anilido derivative,  .

Properties of Di- or Trimolecular Cyanmethylenecarboxylic Ester.—The crystalline substance formed in all the reactions discussed above melts, when thoroughly purified by crystallizing from benzene, at 122°. It is very sparingly soluble in cold ether and ligroin, and quite soluble in chloroform and hot benzene. Acetone, acetic ether, and especially hot alcohol, dissolve it freely, but gradually act upon it. The molecular weight determinations by the freezing-point method in benzene, given by Errara and Perciabosco,[1] agree with the trimolecular formula  (theory = 333).

These determinations were repeated with the following results, which agree better with the dimolecular formula (222), and which prove that Errara and Perciabosco worked in one case with a supersaturated solution:

[1] Ber. d. chem. Ges., 33, 2981.

	I.	II.
Weight of substance	0.0963 gram	0.1381 gram
" " benzene	17.4313 "	26.5160 "
Depression of freezing-point	0°.120	0°.116
Molecular weight found	225	220

	III.	IV.
Weight of substance	0.2550 gram	0.3586 gram
" " benzene	26.5160 "	30.6115 "
Depression of freezing-point	0°.182	0°.180
Molecular weight found	258	317

Determinations I. and II. only are reliable, since solutions III. and IV. were proved to be supersaturated as follows: Solution III. was cooled to its freezing-point and maintained at this temperature (as indicated by a Beckmann thermometer) for ten minutes. Thereupon, 10 cc. of the supernatant liquid were transferred to a weighed dish and the following results obtained by evaporation to dryness. Volume of solution = 10 cc.; sp. gr. of benzene at 5° = 0.8885; weight of benzene used = 8.885 grams; weight of solid residue = 0.0826 gram. From these data it is clear that 0.0092 gram of substance dissolve in 1 gram of benzene at 5°. In one of the molecular weight determinations given by Errara and Perciabosco, 0.01157 gram of substance to 1 gram of benzene were used, therefore the solution in this case was supersaturated. In the other molecular weight determination given by them an exactly saturated solution was used.

In view of these data, molecular weight determinations were carried out by the boiling-point method, using McCoy's apparatus,[1] and the following very curious results were obtained:

	I.	II.
Weight of substance	0.5088 gram	0.6042 gram
Volume of benzene	18 cc.	24.1 cc.
Elevation of boiling-point	0°.210	0°.190
Molecular weight found	441	443

	III.	IV.
Weight of substance	0.6042 gram	0.5676 gram
Volume of benzene	26 cc.	23.7 cc.
Elevation of boiling-point	0°.155	0°.161
Molecular weight found	491	490

[1] Am. Chem. J., **23**, 353.

The only experimental evidence, therefore, which exists at present in favor of Errara and Perciabosco's trimolecular formula is the conversion of the compound by saponification and subsequent loss of carbon dioxide into known trimethylene derivatives as mentioned above.

In conclusion, the writer wishes to express her most grateful appreciation to Dr. Nef for his kindness, for his numerous suggestions, and for the unvarying patience and constant interest with which he followed the progress of this work.